

AD-A183 659 NEW MATERIALS FOR ELECTROCHEMICAL CELLS(U) OXFORD UNIV  
(ENGLAND) INORGANIC CHEMISTRY LAB

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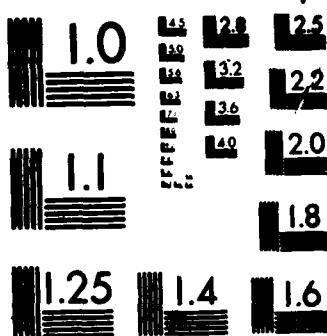
J B GOODENOUGH ET AL. 20 JUN 87 AFOSR-TR-87-0936

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## REPORT DOCUMENTATION PAGE

1a. CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE S AUG 06 1987		Approved for public release; Distribution unlimited	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Ce D		5. MONITORING ORGANIZATION REPORT NUMBER(S) AFOSR TR 87-0936	
6a. NAME OF PERFORMING ORGANIZATION University of Oxford		6b. OFFICE SYMBOL (If applicable)	
7a. NAME OF MONITORING ORGANIZATION AFOSR		7b. ADDRESS (City, State and ZIP Code) Bldg 410 Bolling AFB DC 20332-6448	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Air Force Office of Scientific Research		8b. OFFICE SYMBOL (If applicable) NC	
9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER AFOSR 83-0052		10. SOURCE OF FUNDING NOS.	
11. TITLE (Include Security Classification) New Materials for electrochemical cells		PROGRAM ELEMENT NO. 61102F	PROJECT NO. 2303
12. PERSONAL AUTHORIS Prof. J.B. Goodenough & Dr. P.G. Dickens		TASK NO. A1	WORK UNIT NO.
13a. TYPE OF REPORT Final	13b. TIME COVERED FROM 1983.1.1 TO 1986.12.31	14. DATE OF REPORT (Yr., Mo., Day) 1987.6.20	15. PAGE COUNT 8
16. SUPPLEMENTARY NOTATION			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB GR	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)			
Thermochemical, structural and basic electrochemical properties have been determined for the hydrogen insertion compounds of $V_2O_5$ , $V_{60}I_3$ , $VO_2$ , $Mo_2W_{1-y}O_3$ , $ReO_3$ and for both hydrogen and lithium insertion into the uranium oxides $U_3O_8$ , $\alpha$ -, $\gamma$ - and $\delta$ - $UO_3$ .  The lithium insertion and extraction reactions of ternary oxides $Li[M_2]O_4$ with the spinel framework have been studied for $M = V$ , $Mn$ , $Fe$ , $Ti$ . Attempts to design new lithium cell cathode materials have centred on the thiospinels $Li_{1-x}[M_2]S_4$ where $M = Zr$ and $Ti$ .			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS <input type="checkbox"/>		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL JOHN S. WILKES		22b. TELEPHONE NUMBER (Include Area Code) (202) 767-4960	22c. OFFICE SYMBOL AFOSR/NC
E 4			
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## COMPLETED PROJECT SUMMARY

1. TITLE: New Materials for Electrochemical cells

2. PRINCIPAL INVESTIGATORS: Prof. John B. Goodenough

Dr. P.G. Dickens  
 Inorganic Chemistry Laboratory  
 University of Oxford  
 Oxford, OX1 3QR  
 ENGLAND

3. INCLUSIVE DATES: 1 Jan. 1983 - 31.Dec. 1986

4. GRANT NUMBER: AFOSR-83-0052

5. COSTS AND FY SOURCE: \$43184, FY83; \$35112, FY84;  
 \$47974, FY85; \$59892, FY86;

6. SENIOR RESEARCH PERSONNEL:

B. Ellis  
 S. Hibble  
 S. Pericard  
 R.A. Burnham  
 M.T. Weller  
 A. Manthiram  
 T. Murugesan  
 S. Crouch-Baker  
 D.A. Claridge

7. JUNIOR RESEARCH PERSONNEL:

G.S. James  
 M.G.S.R. Thomas  
 S.A. Kay  
 A.M. Chippindale  
 A.V. Powell  
 W.D. Macklin

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9. PATENTS

No patents were applied for under this grant.

10. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

The research had two main aims: (i) determination of the thermochemical, structural and electrochemical properties of insertion compounds and materials showing mixed electronic/ionic conduction, and (ii) the design, preparation and characterisation of new materials for use as electrolytes or cathode materials in solid state cells. The progress of this research has been described in the series of scientific reports and renewal proposals submitted during the research period and discussed in detail through the scientific publications listed above.

New ambient-temperature lithium and hydrogen insertion compounds have been prepared from the uranium oxides  $\text{U}_3\text{O}_8$ ,  $\text{UO}_2$  and  $\text{UO}_3$ . Electrochemical and thermochanical parameters have been determined for these phases and also for the hydrogen insertion compounds of  $\text{V}_2\text{O}_5$ ,  $\text{V}_6\text{O}_{13}$ ,  $\text{VO}_2$ , the mixed molybdenum-tungsten trioxides ( $\text{Mo}_y\text{W}_{1-y}\text{O}_3$ ) and new structural modifications of  $\text{MoO}_3$  and  $\text{MoO}_2$ ; the phase previously known as "hexagonal  $\text{MoO}_3$ " has been shown to be a partially deammoniated and dehydrated ammonium decamolybdate. Where necessary this work has been accompanied by structural studies to locate the preferred insertion sites, and our understanding of the principles of

hydrogen and ammonium insertion into oxide lattices has been summarised in two recent conference papers.

The dynamics of mobile inserted species is another area of research which is central to the evaluation of materials for electrochemical-cell applications. The techniques of a.c.-conductivity and solid-state pulse nmr have been applied to the characterisation of lithium-ion motion in the battery cathode materials  $\text{Li}_{1-x}\text{CoO}_2$  and  $\text{Li}_x\text{MoO}_3$ , and proton motion in the polymer electrolyte Nafion, in electrochromic materials ( $\text{H}_x\text{WO}_3$ ) and other materials of potential interest as solid-state proton conductors (phosphotungstic acid,  $\text{HTa}(\text{Nb})\text{O}_3$ ,  $(\text{H}_2\text{O})_x\text{H}_2\text{Ta}_2\text{O}_6$ ).

The design of new cathode materials has centred on materials with the spinel framework. Studies on the lithium insertion and extraction reactions of manganese oxo-spinels have proved of both scientific and technological significance, demonstrating the relationship between the  $\text{Li}_{1+x}[\text{Mn}_2]\text{O}_4$  system and the " $\gamma$ - $\text{MnO}_2$ " of a partially discharged  $\text{Li}/\gamma\text{-MnO}_2$  dry cell.

Low-temperature preparations of the spinels  $\text{Li}[\text{V}_2]\text{O}_4$  and  $\text{Li}[\text{Ni}_2]\text{O}_4$  have been demonstrated, via lithium extraction from the layered oxides  $\text{LiVO}_2$  and  $\text{LiNiO}_2$ . The layered oxides  $\text{LiVO}_2$  and  $\text{LiCoO}_2$  have already been established as potentially valuable cathode materials.

Although the 3-D network of interstitial sites in the spinel framework permits diffusion of lithium ions, the room-temperature  $\text{Li}^+$  ion mobility in an oxo-spinel framework is only adequate for low-power applications. In general, lithium-ion mobilities are higher in sulphide lattices. Therefore much attention has been paid to the thio-spinel framework. Lithium thio-spinels have been successfully prepared by the extraction and replacement of copper ions in  $\text{Cu}[\text{Zr}_2]\text{S}_4$  and  $\text{Cu}[\text{Ti}_2]\text{S}_4$ .

A study of the low-temperature molten-salt system Aluminium Chloride- 1-Methyl-3-ethyimidazolium Chloride has revealed that a maximum  $\text{LiCl}$  solubility of 12 mole-per-cent occurs in the room-temperature melt containing 0.62 mole-fraction of  $\text{AlCl}_3$ . This composition has been shown to be stable against the thiospinel  $\text{Li}_x\text{Cu}_{0.1}[\text{Ti}_2]\text{S}_4$  and the layered oxide  $\text{Li}_{1-x}\text{CoO}_2$ . A working cell with these two electrodes is calculated to give an open circuit voltage of about 1.8V, and such a cell was being constructed at the close of the contract period.

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